

PATENT SPECIFICATION

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(54) PROCESS FOR PREPARING A COPOLYMER OF TRIOXANE

(71) We, FARBWERKE HOECHST AKTIENGESELLSCHAFT, formerly Meister Lucius & Brüning, a Body Corporate recognised under German Law, of 6230 Frankfurt (M)-Hoechst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The present invention provides a process for preparing copolymers of trioxane.

It is possible to polymerize trioxane and to copolymerize it with cyclic ethers in substance, in the melt, in the gaseous phase, in suspension and in solution. The cationic polymerization in substance at a temperature exceeding the melting point of monomeric trioxane (62°C) is especially interesting. Several discontinuous and continuous embodiments of that polymerization process have already been disclosed. German Patent Specification No. 1,137,215, laid open to public inspection, discloses *inter alia* the polymerization on an endless conveyor band and Belgian Patent No. 585,980 discloses the continuous polymerization carried out in containers made of plastic materials, for example of polyethylene. The last-mentioned process has many advantages, for example an easy dissipation of polymerization heat and the possibility of polymerizing in any layer thickness desired; moreover, this process can be carried out without heavy technical expenditure, although, after the polymerization, the polymeric trioxane has to be removed from the polyethylene containers by a separate operation. The same drawbacks are inherent in the process disclosed in German Patent Specification No. 1,225,398 laid open to public inspection.

The present invention provides a process of preparing a copolymer of trioxane in which a mixture comprising 50% to 99.9% by weight of trioxane and 0.1% to 50% by weight of a cyclic ether and/or a cyclic acetal is polymerized in the melt in the presence of 0.0001% to 1.0% by weight of a

cation-active catalyst at a temperature within the range of 62°C (melting point of trioxane) to 115°C (boiling point of trioxane) in a container made from a thermoplastic material, which process comprises carrying out the polymerization of said mixture in a container made from a film or sheet of an oxymethylene polymer having a crystalline melting point preferably within the range of 120°C to 180°C and a thickness preferably within the range of 0.01 millimetre to 1.0 millimetre, and subsequently working up the polymer together with the film or sheet.

By operating according to the process of the invention, the polymerization containers need not be removed prior to the work-up. The process is substantially less complicated; for, hitherto, removing the polymerization containers, for example when polyethylene was used as the container material, required not only a separate operation but also special care, since polyethylene is insoluble under the work-up conditions so that even small amounts of this material cause coggings in the pumps and dies. Moreover, these proportions of polyethylene are inhomogeneously mixed into the finished product, thus having a very detrimental effect on its mechanical properties; this drawback is also avoided by the process of the invention.

The polymerization according to the process of the invention can be carried out discontinuously or continuously. For a discontinuous polymerization, for example, flat bags or sacks made of polyacetals may be filled with molten trioxane and the comonomer, and after the catalyst has been added, these bags may be introduced into a thermostat. The continuous polymerization may be carried out by suspending flat bags made of oxymethylene polymers from a moving band or rope in such a manner that they can be continuously charged with liquid trioxane, the comonomer and the catalyst by means of a dosing device and they are then passed through an air—or liquid bath having a certain temperature, and—after the

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polymerization—into a hydrolysis vessel. The continuous polymerization may also be carried out in flat pipes made of oxymethylene polymers instead of bags. These pipes 5 may be produced by welding two strips together or directly by blow extrusion.

The oxymethylene polymers may be a homopolymer of formaldehyde or trioxane, the terminal groups of which are blocked, 10 for example by esterification or etherification, it may also be a copolymer of formaldehyde or trioxane, preferably a copolymer of trioxane with a cyclic ether or cyclic acetal, for example, with 0.1% to 15% by 15 weight of ethylene oxide or with dioxolane. The oxymethylene polymers used as container materials must, of course, be insoluble in the mixture of the monomers under the reaction conditions. Oxymethylene 20 polymers, the crystallite melt points of which are within the range of 120°C to 180°C, preferably 145°C to 170°C, are preferred. For preparing the pipes suitable as polymerization containers, terpolymers of 25 trioxane are preferably used.

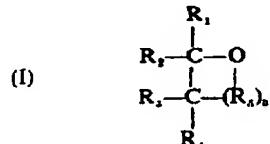
Especially preferred for the containers are films or sheets made from terpolymers of from 98.99% to 89.0% by weight of trioxane, from 1% to 10% by weight of a cyclic ether and/or a cyclic formal and from 0.01% to 1% by weight of a butanediol diglycidyl ether, as well as films or sheets made from terpolymers of from 99.9% to 80% by weight of trioxane, up 30 to 10% by weight of a cyclic ether and from 0.1% to 10% by weight of a triol-formal, preferably hexane-triol formal.

In comparison with films or sheets made from formaldehyde- or trioxane-homopolymers, the terpolymers have the advantage of being more easily soluble when worked up in solution or more readily miscible with the polymer prepared when worked up in the melt.

45 The copolymerization is carried out in the melt at a temperature in the range of from the melting point of trioxane (62°C) to the boiling point thereof (115°C) and is catalysed by the known cation-active catalysts. Suitable catalysts are, for example, inorganic or organic acids, acid halides and, especially Lewis-acids (defined by Kortüm, Lehrbuch der Elektrochemie, Wiesbaden 1948, pages 300 and 301), among which 50 boron fluoride and its complex compounds, for example boron fluoride ethers, are very well suitable. Especially useful are the diazonium fluoroborates proposed in Belgian Patent Nos. 503,648 and 618,213 55 and the compounds proposed in Belgian Patent No. 585,980. The concentration of the catalyst may vary within wide limits. It depends on the nature of the catalyst chosen and on the molecular weight intended for the polymer to be prepared.

It is within the range of 0.0001% to 1% by weight, preferably 0.001% to 0.1% by weight, calculated on the monomer mixture. Since these catalysts tend to decompose the polymer, it is advisable to deactivate them immediately after the polymerization, for example, by means of ammonia.

As comonomers for trioxane there are used cyclic ethers and/or cyclic acetals, for example, compounds of the general formula 75 (I)



in which R₁ to R₄ are identical or different, each representing a hydrogen atom, an alkyl radical or an alkyl radical substituted by up to 3 halogen atoms, R₂ represents a methylene- or oxymethylene radical or a methylene- or oxymethylene radical substituted by one or two alkyl groups which may be substituted groups n representing zero or an integer of from 1 to 3, or R₃ represents the radical $-(O-CH_2-CH_2)_n-OCH_2-$, n representing 1 and m representing an integer of from 1 to 3. The abovementioned alkyl radicals contain from 1 to 5 carbon atoms and may be substituted by 0 to 3 halogen atoms, preferably chlorine atoms.

As cyclic ethers or cyclic acetals there are especially useful ethylene oxide, glycol formal and diglycol formal. Furthermore, propylene oxide, epichlorohydrin and 4-chloromethyldioxolane may also be used.

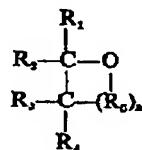
Finally, there are also useful cyclic or linear formals of long chain α,ω -diols, for example, butane-diol formal or hexane-diol formal.

It is possible to copolymerise from 0.1% to 50%, preferably from 0.1% to 10% by weight of these comonomers with trioxane.

The polymerization containers and the polymer contained therein may be simultaneously crushed or pulverized in various ways, for example, in a cross beater mill.

The work-up consists in neutralizing the catalyst, removing the residual monomers and reducing the unstable terminal groups to a single comonomer component. When boron trifluoride or its complex compounds are used as the preferred catalysts, the neutralization may be effected by suspending the crude polymer in a liquid suspension medium containing a base, for example, ammonia or an amine, for example, triethylamine or cyclohexylamine. The amount of the base depends on the catalyst concentration and generally ranges from 0.1% to 2% by weight, calculated on the polymer.

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5	The neutralization is preferably effected in a suspension medium which is also a solvent for the monomers, for example, methylene chloride, cyclohexane or especially mixtures of water and methanol, since then the residual monomers are removed by the same operation.	freshly distilled liquid trioxane and 3 grams of ethylene oxide were added thereto. The bag was closed and then hung for 20 minutes in a water bath having a temperature of 80°C and subsequently worked up in the manner disclosed in Example 1. The yield was 92.1%; the reduced specific viscosity was 0.81 dl/gram (measured in γ -butyrolactone + 2% of diphenyl amine at 140°C).
10	The unstable terminal groups are subjected to a thermal degradation either in solution, preferably in an alkaline medium, or in the melt. Suitable solvents are, for example, mixtures of alcohol and water or benzyl alcohol at a temperature within the range of 120°C to 180°C, to which solvents from 0.01% to 2% by weight of amines, for example ammonia, triethyl amine or triethanol amine, may be added to accelerate the degradation. For the degradation of the unstable terminal groups in the melt, the polymer is kneaded in an appropriate vessel at a temperature exceeding its melting point, advantageously in the presence of a stabilizer, for example, a phenol or a combination of aromatic amine with a (poly)-amide. This degradation in the melt can be accelerated by adding from 0.01% to 2% by weight of an amine, for example, ammonia, triethyl amine or triethanol amine or a solution thereof in water or a mixture of alcohol and water.	freshly distilled liquid trioxane and 3 grams of ethylene oxide were added thereto. The bag was closed and then hung for 20 minutes in a water bath having a temperature of 80°C and subsequently worked up in the manner disclosed in Example 1. The yield was 92.1%; the reduced specific viscosity was 0.81 dl/gram (measured in γ -butyrolactone + 2% of diphenyl amine at 140°C).
15	The products prepared according to the process of the invention can be thermoplastically processed into shaped articles.	Example 3 A bag made of a terpolymer of trioxane, ethylene oxide and hexane-triol formal (weight ratio 97.9:2.0:0.1), having a wall thickness of 70 μ , was filled with 100 millilitres of freshly distilled liquid trioxane and 2 grams of ethylene oxide and 15 milligrams of boron fluoride dibutyl etherate were added thereto by means of a syringe. The bag was closed and hung for 20 minutes in a water bath having a temperature of 72°C and subsequently worked up in the manner disclosed in Example 1. The yield was 90.8%; the reduced specific viscosity was 0.77 dl/gram (measured in γ -butyrolactone + 2% of diphenyl amine at 140°C).
20	The following Examples illustrate the present invention.	WHAT WE CLAIM IS:— 1. A process of preparing a copolymer of trioxane by the polymerization in the melt of a mixture comprising 50% to 99.9% by weight of trioxane and 50% to 0.1% by weight of a cyclic ether and/or cyclic acetal in the presence of 0.0001% to 1.0% by weight of a cation-active catalyst at a temperature within the range of the melting point to the boiling point of trioxane in a container made from a thermoplastic material, which process comprises carrying out the polymerization in a container made from a film or sheet of an oxymethylene polymer and subsequently working up the polymer together with the film or sheet.
25		100
30		95
35		90
40	<i>Example 1</i> 20 milligrams of <i>p</i> -nitrophenyl-diazonium-fluoroborate were put in a bag made of a copolymer of trioxane and ethylene oxide (weight ratio 98:2), having a wall thickness of 50 μ , and then 100 millilitres of freshly distilled liquid trioxane and 2 grams of ethylene oxide were added thereto. The bag was closed and subsequently introduced into a drying cabinet at 70°C and after 30 minutes it was dissolved in 1 litre of benzyl-alcohol containing 10 millilitres of triethanol amine, at a temperature of 150°C. After 30 minutes the perfectly clear solution was allowed to cool, the precipitated copolymer was filtered with suction, boiled with methanol and dried <i>in vacuo</i> . The yield was 90.6% of the theoretical yield; the reduced specific viscosity was 1.38 dl per gram (measured in γ -butyrolactone + 2% of diphenyl amine at 140°C).	105
45		100
50		95
55		90
60	<i>Example 2</i> 20 milligrams of <i>p</i> -nitrophenyl-diazonium-fluoroborate were put in a bag made of a terpolymer of trioxane, ethylene oxide and butane-diol diglycidyl ether (weight ratio 97.95:2.0:0.05), having a wall thickness of 50 μ , and subsequently 140 millilitres of	110
		115



in which R₁ to R₄ are identical or different, each representing a hydrogen atom, an alkyl radical or an alkyl radical substituted by up to 3 halogen atoms, and R₄ represents a methylene- or oxymethylene radical or a methylene or oxymethylene radical substituted by one or two alkyl groups which may be halogen substituted, n being zero or an integer of from 1 to 3, or R₄ represents

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	the radical $-(O-CH_2-CH_2)_n-OCH_3$, n being 1 and m being an integer of from 1 to 3, the alkyl radicals containing 1 to 5 carbon atoms.	wherein an etherate of boron fluoride is used as catalyst.
5	3. A process as claimed in claim 2, wherein ethylene oxide, glycol formal, diglycol formal, propylene oxide, epichlorohydrin or 4-chloromethyl dioxolane is used as comonomer.	17. A process as claimed in any one of claims 1 to 16, wherein the catalyst is deactivated immediately after the polymerization.
10	4. A process as claimed in any one of claims 1 to 3, wherein a cyclic or linear formal of a long chain α,ω -diol is used as comonomer.	18. A process as claimed in any one of claims 1 to 17, wherein deactivation of the catalyst is carried out by suspending the polymer in a liquid suspension medium containing a base.
15	5. A process as claimed in claim 4, wherein butane-diol formal or hexane-diol formal is used as comonomer.	19. A process as claimed in claim 18, wherein ammonia or an amine is used as the base.
20	6. A process as claimed in any one of claims 1 to 5, wherein the amount of the comonomer polymerized with trioxane is within the range of 0.1% to 10% by weight.	20. A process as claimed in claim 18 or claim 19, wherein the base is present in an amount within the range of 0.1% to 2% by weight, calculated on the polymer.
25	7. A process as claimed in claim 6, wherein the film or sheet is made from a copolymer of trioxane and a cyclic ether or cyclic acetal.	21. A process as claimed in any one of claims 18 to 20, wherein the suspension medium is a solvent for the monomers.
30	8. A process as claimed in claim 7, wherein the film or sheet is made from a copolymer of trioxane with 0.1% to 15% by weight of ethylene oxide or with dioxolane.	22. A process as claimed in claim 21, wherein the suspension medium used is methylene chloride, cyclohexane or a mixture of methanol and water.
35	9. A process as claimed in any one of claims 6 to 8, wherein the film or sheet is made from a terpolymer.	23. A process as claimed in any one of claims 1 to 22, wherein the unstable terminal groups are subjected to a thermal degradation in solution.
40	10. A process as claimed in claim 9, wherein the film or sheet is made from a terpolymer of from 98.99% to 89% by weight of trioxane, from 1% to 10% by weight of a cyclic ether and/or a cyclic formal and from 0.01% to 1% by weight of butane-diol diglycidyl ether or made from a terpolymer of from 99.9% to 80% by weight of trioxane, up to 10% by weight of a cyclic ether and from 0.1% to 10% by weight of a triol-formal.	24. A process as claimed in claim 23, wherein the solvent used for the thermal degradation is a mixture of alcohol and water or benzyl alcohol, used at a temperature of 120°C to 180°C.
45	11. A process as claimed in claim 10, wherein the said triol-formal is hexane-triol formal.	25. A process as claimed in claim 23 or 24, wherein the solvent used for the thermal degradation is used in conjunction with 0.01% to 2% by weight of ammonia or an amine as degradation accelerator.
50	12. A process as claimed in any one of claims 1 to 11, wherein the oxymethylene polymer has a crystallite melting point of 120°C to 180°C.	26. A process as claimed in any one of claims 1 to 22, wherein the unstable terminal groups are subjected to thermal degradation in the melt.
55	13. A process as claimed in any one of claims 1 to 11, wherein the catalyst is used as a concentration within the range of 0.001% to 0.01% by weight, calculated on the monomer mixture.	27. A process as claimed in claim 26, wherein 0.01% to 2% by weight of an amine or ammonia as degradation accelerator is incorporated into the melt.
60	14. A process as claimed in any one of claims 1 to 13, wherein as catalyst there is used an inorganic or organic acid, an acid halide or a Lewis acid.	28. A process as claimed in claim 25 or claim 27, wherein triethyl amine or triethanol amine is used as degradation accelerator.
65	15. A process as claimed in claim 14, wherein boron fluoride or a complex compound thereof is used as a catalyst.	29. A process as claimed in claim 1, carried out substantially as described in any one of the Examples herein.
	16. A process as claimed in claim 15.	30. A copolymer of trioxane, whenever prepared by a process as claimed in any one of claims 1 to 29.

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